THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

I. STUDIES ON REACTIONS OF OPTICALLY ACTIVE COMPLEXES WITH OPTICALLY ACTIVE COORDINATING GROUPS

II. STEREOISOMERS OF THE DICHLORO BIS ETHYLENEDIAMINE PLATINUM (IV) ION

BY

LEO FRANCIS HENEGHAN

B.S., Illinois College, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

I. STUDIES ON REACTIONS OF OPTICALLY ACTIVE COMPLEXES WITH OPTICALLY ACTIVE COORDINATING GROUPS

Introduction

During recent years the researches of Bailar and co-workers have built up evidence for the very interesting phenomenon of "Preferential Coordination". In some cases the ability of one isomer of a racemic mixture to enter the coordination sphere of inorganic complexes containing optically active groups is sufficiently different from that of the other isomer so as to permit partial resolution of the racemic mixture. With other racemic mixtures; e.g., racemic amino acids, preferential coordination is not exhibited. The work reported in this thesis was undertaken because additional information on the coordinating abilities of the optical isomers of a racemic amino acid was needed. Tyrosine was chosen as the amino acid to be investigated. There seemed to be two logical ways to attack the problem:

(1) Attempt to resolve tyrosine with *bis-levo*-propylenediamine complexes of cobalt

(2) Study the rate of reaction of $[Co\ l\text{-}pn_2(H_2O)(OH)]Cl_2$ with each isomer of the amino acid separately in order to obtain quantitative information on the stabilities of the complexes of *dextro*- and *levo*-tyrosine.

Experimental and Discussion

In the first set of reactions studied $[Co\ l\text{-}pn_2Cl_2]Cl$ was allowed to react with a one-hundred percent excess of racemic tyrosine. If the stabilities of $[Co\ l\text{-}pn_2l\text{-}tyro]Cl_2$ and $[Co\ l\text{-}pn_2d\text{-}tyro]Cl_2$ are sufficiently different then, in the

presence of excess amino acid, the less stable complex should give way to the more stable one giving at least a partial resolution of the amino acid. It was apparent, however, that under the experimental conditions of concentration, temperature and pH employed in these experiments, one form of racemic tyrosine entered the coordination sphere of a *bis-levo*-proplyenediamine complex of cobalt just as readily as did the other.

Although the two isomers of tyrosine apparently enter the coordination sphere with equal ease, resolution might possibly be attained by preferential displacement of one isomer from the complex by *levo*-propylenediamine. This would be possible only if the stabilities of the complexes involved, [Co *l*-pn_2*l*-tyro]Cl_2 and [Co *l*-pn_2*d*-tyro]Cl_2, are sufficiently different to permit such a preferential displacement. This hypothesis was tested experimentally. Apparently the stability of the complex containing *levo*-tyrosine is so similar to that of the complex containing *dextro*-tyrosine that differences in the displacement of the isomers cannot be observed. This is in complete agreement with the observations on preferential coordination.

Quantitative data on the coordinating abilities of the two isomers of tyrosine was obtained by determining the rate of coordination of each isomer separately with hydroxo-aquo-*bis-levo*-propylenediamine cobalt (III) chloride, [Co *l*-$pn_2(H_2O)$-(OH)]Cl_2. Periodically aliquot portions of the two solutions were removed and the optical densities of these samples measured with a Beckman spectrophotometer. From these values the concentrations of the reactant [Co *l*-$pn_2(H_2O)$-(OH)]Cl_2, and product, [Co *l*-pn_2 *d*-or-*l*-tyro]Cl_2, were calculated by the method of Gibb (1). The changes in the concentrations of the reactant and product with time were measured at 60° and 70° Centigrade. The rate of reaction at 40° was found to be too slow and the rate at 80° too rapid to permit accurate determination of the changes in concentrations by this method. It was then apparent that *levo*-tyrosine entered the coordination sphere more readily than did *dextro*-

tyrosine. However, it was also apparent that the coordinating abilities were too similar to permit resolution of the amino acid by this means.

The α-amino acids have relatively strong powers of coordination and form stable complexes with cobalt. This strong tendency apparently overcomes the slight preference that the complex has for one form of the antipode with the result that, if both forms are available, either form will coordinate equally as well with a cobalt complex containing *levo*-propylenediamine.

II. STEREOISOMERS OF THE DICHLORO BIS-ETHYLENEDIAMINE PLATINUM (IV) ION

Introduction

Several investigators (2,3) have attempted to prepare the stereoisomers of the dichloro *bis*-ethylenediamine platinum (IV) ion but met with little success. In each case what was thought to be the *trans* isomer was prepared without difficulty but no definite proof was extended to show that the corresponding *cis* isomer had been obtained. If a satisfactory synthesis for the *cis* isomer could be developed, the way would be open for further investigations, not only with this but with similar ions containing other negative groups or other diamines.

Experimental and Discussion

The usual method for changing the *trans* isomer of a compound such as $[Pt\ en_2\ Cl_2]Cl_2$ to the corresponding *cis* isomer involves conversion to the carbonato derivative with silver carbonate followed by treatment with alcoholic hydrogen chloride. The carbonato group is known to occupy *cis* positions as it is not capable of spanning *trans* positions. The alcoholic hydrogen chloride converts the carbonato to the

dichloro without permitting rearrangement back to the *trans* configuration. However, in the case of the platinum complexes, the coordinated chloro groups are so firmly held by the central metal ion that they are not removed even upon extended grinding with silver carbonate. Similar experiments were carried out with *trans* [Pt en_2 Br_2]Br_2. The bromide ion, being larger than the chloride ion, should be less firmly held by the central platinum ion. Also, the greater insolubility of the silver bromide over that of silver chloride should favor the conversion to the carbonato derivative. All of the bromide was successfully removed from the coordination sphere; however, the desired compound, [Pt en_2 CO_3]CO_3, could not be isolated from the reaction mixture. If the carbonato salt is a product of this reaction, it is apparently too unstable to be isolated from solution.

A successful method was developed, however, for the direct synthesis of *cis* [Pt en_2 Cl_2]$(NO_3)_2$ using [Pt en Cl_2] and [Pt en $(OH)_2Cl_2$] as intermediate products. Upon comparison of the colors, the solubilities and the x-ray diffraction patterns it was apparent that this product was not the same as the known *trans* compound. Since the *cis* compound may exhibit optical isomerism while the *trans* cannot, a conclusive proof that the product does possess the *cis* configuration would lie in the resolution of this material. The product was successfully resolved using ammonium-*d*-α-bromocamphor-π-sulfonate as the resolving agent. The optical rotations of the fractions isolated did not correspond to the rotation that would be expected assuming that the activity was due to the presence of the resolving agent alone. The active product was then racemized by boiling its aqueous solution.

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VITA

The author was born in Jacksonville, Illinois, on October 29, 1923. He received his elementary and secondary education in the public schools of that city, graduating from Jacksonville High School in June, 1941. His undergraduate training was received at Illinois College where he was awarded the degree of Bachelor of Arts in June, 1946. He entered the Graduate School of the University of Illinois in September, 1946. Regular residence has continued from that date to the present. In this period he held teaching and research assistantships.

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